Polarographic Study of Proline Complexes of Copper and Zinc

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Proline complexes of copper and zinc were studied polarographically in KNO_3 medium. The reduction was found to be quasireversible nature. The stability constants evaluated using formal potentials were $\beta_1 = 2.0 \times 10^{11}$ and $\beta_2 = 3 \times 10^{15}$ for copper and $\beta_1 = 1.5 \times 10^5$ $\beta_2 = 1.1 \times 10^9$ and $\beta_3 = 1.3 \times 10^{12}$

In our previous paper(1) we have reported results of study of proline complexes of cadmium and indium. This paper presents the data obtained on copper and zinc complexes.

EXPERIMENTAL

A balancing type manual polarograph was set up to obtain current potentials curves. A saturated calomel electrode (SCE) was used as the reference electrode. Measurements were made 30 ± 0.1°C, using a water thermostat. Ionic strength was maintained at 0.5M using potassium nitrate. pH of the test solution was varied and measured with EC-Expando metric pH meter. Gelatin was used as a maximum supressor at a concentration of 0.002%.

Dilute amalgam of copper and zinc were prepared by controlled potential electrolysis using a mercury pool cathode. Proline (E. Merck) was used without further purification. All other chemicals used were analytical grade and the currents reported were corrected for residual current.

RESULTS AND DISCUSSION

COPPER - COMPLEXES

A well-defined wave was obtained for copper in 0.5M potassium nitrate ($E_{1/2}$ = + 0.020 V vs. SCE). Polarograms of copper were recorded in the presence of proline at different pH in 0.5M potassium nitrate. Shift in the half-wave potential indicated complexation. However the slope of the log plots suggested a quasi-reversible reduction (slope > 32). The diffusion controlled nature of reduction was however ascertained by the effect of height of mercury column and the concentration of the depolariser on the diffusion current.

Composite polarograms were obtained using a dropping amalgam electrode in solutions containing copper and proline at different pH. Prolinate ion concentration was calculated from pH of the test solution and dissociation constant of proline (10.25) obtained using pH titration method(2). The values of formal potentials, $E_f°$, defined as the midpoints of the symmetrical anodic-cathodic waves were recorded as the function of pA (-log prolinate concentration) (Table 1).

The plot of $E_f°$ (Equivalent to reversible half-wave potentials) vs. pA resulted in a smooth curve indicating presence of different species whose stabilities do not differ appreciably. The method suggested by DeFord and Hume(3) was therefore applied to obtain stability constants.

The Table 2 gives values of various F_j functions. Two complexes could be identified with the stability $\beta_1 = 2.0 \times 10^{11}$ and $\beta_2 = 3.0 \times 10^{15}$ The values obtained show a close resemblance with data presented by Li and Doody(5). The apparent difference may be because of lower ionic strength and buffers used by them resulting into enhancement in the stability.

TABLE 1

COPPER PROLINE SYSTEM : EFFECT OF pH

$(Cu^{2+}) = 0.1mM$, $KNO_3 = 0.5M$,
$m^{2/3} t^{1/6} = 1.80\ mg^{2/3}\ sec.^{-1/2}$ $E_{1/2}$ (S) = 0.20 V
i_d = 2.60 µA

	$E_{1/2}$		i_d			$E_f°$
pH	pA	-V vs. SCE	µA	pH	pA	-V vs. SCE
7.50*	4.45	0.257	2.52	7.95	4.30	0.209
8.03	4.22	0.260	2.47	8.23	4.02	0.212
8.28*	3.67	0.263	2.46	8.54	3.72	0.225
8.49*	3.47	0.267	2.47	8.79	3.48	0.237
8.84	3.43	0.270	2.48	8.98	3.29	0.245
8.61*	3.35	0.271	2.47	9.20	3.09	0.256
9.01	2.96	0.282	2.45	9.32	2.98	0.265
9.62**	2.55	0.299	2.42	9.50	2.82	0.274
9.66	2.39	0.309	2.48	9.48*	2.58	0.289
9.82*	2.27	0.315	2.42	9.63*	2.41	0.302
9.50+	2.22	0.322	2.40	9.83*	2.26	0.313
				10.11*	2.08	0.325

+ HA = 0.04M ** HA = 0.015M * HA = 0.02M
In all other cases [HA] is 0.01 M.

ZINC-COMPLEXES

The reduction of zinc in 0.5M KNO_3 was found to be reversible with the half-wave potential at -1.000 volts vs. SCE. However, in the presence of complexing agent, reduction was found to be quasireversible (slope > 32). Formal potentials were therefore obtained using a dropping amalgam electrode (Table 3). The plot of E_f° vs pA indicated the presence of more than one complex. Analysis of data by De Ford and Hume's method showed the presence of complexes with the over all stability constants as $\beta_1 = 1.5 \times 10^5$, $\beta_2 = 1.1 \times 10^9$ and $\beta_3 = 1.3 \times 10^{12}$.

CALCULATION OF KINETIC PARAMETERS

The kinetic parameters for the polarographic reduction viz. the standard rate constant, k_s and the transfer coefficient, could be calculated from the current potential curves, provided the standard (or formal) potential is known. For the proline complexes of copper and zinc, these parameters were evaluated by the method of Randles(4).

The current potential relationship for an irreversible reduction is given by

$$i/i_d = 1/2 \left[1 + \tanh \left(-B\eta/2 \right) \phi(H) \right] \quad \ldots\ldots (1)$$

Where i is the current at potential E, i_d is the diffusion current, β is nF/RT, η is the over potential ($E-E_f^\circ$) and ϕ (H) is a function of a parameter H, defined by

$$H = h \tau^{1/2} \quad \ldots\ldots (2)$$

'h' is the another parameter related to the standard rate constant by the expression

TABLE 2

COPPER PROLINE SYSTEM : VALUES OF F_j FUNCTIONS

(Cu^{2+}) = 0.4mM, KNO_3 = 0.5M, $m^{2/3} t^{1/6}$ =1.80
$E_{1/2}$ (S) = 0.0 20V, i = 2.60 uA

pA	F_0 (A)X10^{-7} Exptl.	F_1 (A)X10^{-11}	F_2 (A)X10^{-15}	F_0 (A)X10^{-7} Calcd.
4.0	5.459	5.459	-	5.00
3.8	10.87	6.856	3.06	10.75
3.6	23.40	9.324	2.92	25.06
3.4	55.35	13.90	2.99	56.80
3.2	130.8	20.74	2.97	133.80
3.0	328.7	32.87	3.09	321.00
2.8	765.2	48.28	2.92	791.22
2.6	1982	78.91	3.06	1956
2.4	4978	125.0	3.09	4866
2.2	14350	227.4	3.57	12147

$\beta_1 = 2.0 \times 10^{11}$, $\beta_2 = 3.0 \times 10^{15}$

$$\log \left(\frac{h}{1 + \exp\beta\eta} \right) = \log \left[(3/7D)^{1/2} Ks \right] \frac{\alpha\beta n}{2.303} \quad \ldots (3)$$

where 'D' is the diffusion coefficient. As evident from eq. 3, a plot of log ($h/1+\exp\beta\eta$) vs. η results in a straight line whose slope gives the value of α and intercept (at $\eta = 0$) the value of k_s .

The value i/i_d at different E or n were used to calculate the function ϕ (H) from eq.1. The values of H or h were calculated as a function on n from a plot of ϕ (H) vs H which is available. The values of kinetic parameters, calculated from eq. 3 for copper and zinc are reported in Table 4. The value of standard rate constant was of the order of 3×10^{-3} cm Sec^{-1} .

TABLE 3

ZINC PROLINE SYSTEM : EFFECT OF pH

Zn = 0.4mM, KNO_3 = 0.5M, $m^{2/3} t^{1/6}$ = 1.80 $mg^{2/3}$
$E_{1/2}$ (S) = -1.000V i_d = 2.60 µA

pH	pA	$E_{1/2}$ -V vs. SCE	i_d µA	pH	pA	E_f° -V vs.SCE
8.13•	4.12	1.074	2.35	8.16	4.09	1.038
8.25•	4.00	1.083	2.30	8.28	3.98	1.043
8.83+	3.84	1.090	2.29	8.44	3.82	1.050
8.60•	3.66	1.110	2.30	8.51	3.95	1.052
8.80•	3.47	1.127	2.00	8.65	3.61	1.059
9.00•	3.27	1.146	2.26	8.72	3.54	1.064
9.10•	3.18	1.163	2.16	8.94	3.33	1.068
8.98*	2.99	1.174	2.20	9.10	3.18	1.082
9.18*	2.81	1.192	2.00	9.24	3.05	1.092
9.14•	2.63	1.211	1.80	9.35	2.95	1.094
9.60*	2.44	1.232	1.80	9.73	2.64	1.121
				9.47*	2.55	1.129
				10.03*	1.12	1.170
				10.13*	2.06	1.178

+ HA = .004M • HA = 0.01M * HA = 0.02M
[HA] = 0.01M in all other cases

TABLE 4

VALUE OF KINETIC PARAMETERS : COPPER AND ZINC SYSTEM

	pH	pA	α	-log k_s
	8.28	3.67	0.39	3.26
	8.49	3.47	0.45	3.25
	8.61	3.35	0.48	3.18
COPPER	9.01	2.96	0.52	3.04
	9.62	2.55	0.49	2.67
	9.82	2.27	0.44	2.45
	8.13	4.12	.23	3.15
	8.83	3.84	.26	2.79
ZINC	9.10	3.18	.36	3.20
	9.74	2.63	.60	3.62

REFERENCES

1. S.N. Prabhu, S.S. Kelkan and B.I. Nemade, J. Electrochem Soc.(India), 29.3, (1980) 178.

2. H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.

3. D.D. DeFord and D.N. Hume, J. Am. Chem. Soc., 73, (1951) 5321.

4. J.E.B. Randles, Can. J. Chem. 37, (1959) 238.

5. N.C. Li and E. Doody, J. Am. Chem. Soc., 76, (1954) 221.

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